5

10

15

25

## **CLAIMS:**

- 1. Process for separating lanthanides from one another and/or lanthanides from actinides and/or actinides from one another and/or from other transition metals in an aqueous medium, characterized in that it comprises the following essential steps:
- 1 treatment of the aqueous medium with at least one ligand selected from the group comprising ethylenediaminetetraacetic acid (EDTA) and/or linear or cyclic polyamino acids, preferably linear polyamino acids of formula (I) below:

$$(A^{1})_{a} (R^{1})_{b} C = \begin{bmatrix} N & (CR^{3}_{2})_{i} \\ C(R^{2})_{c} (A^{2})_{d} \end{bmatrix}_{p1} C = R^{4} - C = \begin{bmatrix} N & (CR^{7}_{2})_{h} \\ C(R^{6})_{f} (A^{3})_{g} \end{bmatrix}_{q} C = R^{8}$$

**(I)** 

in which:

- a = 0 or 1 and b = 2 or 3; - c = 2 or 3 and d = 0 or 1;

-p = 0 to 3, preferably 2;

-p1 = 1 to 4, preferably 2 or 3;

-e = 0 or 1:

-q = 1 to 4, preferably 2 or 3;

20 - f = 2 or 3 and g = 0 or 1;

- h and i, which are identical or different, are each 1, 2 or 3, preferably 1 or 2;
- A<sup>1</sup>, A<sup>2</sup> and A<sup>3</sup> are identical to or different from one another and correspond to a monovalent acid group preferably selected from the group comprising:

-COOR, -PO<sub>3</sub>R' and -SO<sub>3</sub>R",

where R, R', R'' = H or a cation;

- the radicals  $R_1$  are identical to or different from one another and correspond to:

 $\Delta H$ 

 $\Delta C_1$ - $C_{10}$  alkyl or

 $\Delta$  R<sup>9</sup>R<sup>10</sup>NC —, where a = 0 and R<sup>9</sup> and R<sup>10</sup> are identical or different and each correspond to hydrogen or a hydrophilic monovalent radical preferably selected from amino and/or (poly)hydroxylated and/or alkoxylated and/or (poly)etherified hydrocarbon radicals, these radicals preferably being of the (cyclo)alkyl, aralkyl, alkylaryl, (cyclo)alkenyl, aralkenyl, alkenylaryl or aryl type.

 $R^9$  and  $R^{10}$  each corresponding even more preferably to a  $C_1$ - $C_{10}$  hydroxyalkyl, a  $C_1$ - $C_{10}$  alkoxy or a polyol, advantageously a hydrogenated saccharide;

- the radicals R<sup>2</sup> are identical to or different from one another;
- the radicals R<sup>3</sup> are identical to or different from one another;
- the radicals R<sup>6</sup> are identical to or different from one another;
- the radicals R<sup>7</sup> are identical to or different from one another,

 $R^2$ ,  $R^3$ ,  $R^6$  and  $R^7$  being identical to or different from one another and corresponding to H or a  $C_1$ - $C_{10}$  alkyl;

- the radicals R<sup>4</sup> are identical to or different from one another and correspond to a hydrophilic divalent group preferably selected from aromatic amino and/or hydroxylated groups, aromatic and alkyl amino and/or hydroxylated groups, aromatic and (cyclo)alkylenic amino and/or hydroxylated groups and (cyclo)alkylenic amino and/or hydroxylated groups,

it being possible for this group to contain alkoxy and/or (poly)ether radicals,

R<sup>4</sup> preferably being a group

5

10

15

20

25

30

$$-R^{13} \longrightarrow R^{14} \longrightarrow R^{13}$$

where R<sup>13</sup> is an amino group and R<sup>14</sup> is a C<sub>1</sub>-C<sub>4</sub> alkylene;

- the divalent group R<sup>5</sup> is an alkylene, preferably CH<sub>2</sub>, or a group having the same definition as R<sup>4</sup>: or
- the group R<sup>8</sup> corresponds to a hydroxyl, to A<sup>4</sup> having the same definition as A<sup>1</sup>, A<sup>2</sup> and A<sup>3</sup>, to hydrogen or to -NR<sup>9</sup>R<sup>10</sup>, where R<sup>9</sup> and R<sup>10</sup> are identical

to or different from one another and are a hydrophilic monovalent radical preferably selected from amino and/or (poly)hydroxylated and/or alkoxylated and/or (poly)etherified hydrocarbon radicals, these radicals preferably being of the (cyclo)alkyl, aralkyl, alkylaryl, (cyclo)alkenyl, aralkenyl, alkenylaryl or aryl type,

R<sup>8</sup> even more preferably being a C<sub>1</sub>-C<sub>10</sub> hydroxyalkyl, a C<sub>1</sub>-C<sub>10</sub> alkoxy or a polyol, advantageously a hydrogenated saccharide;

- 2 - (nano)filtration of the aqueous solution treated with the ligand (I), under a transmembrane pressure greater than or equal to 0.01 MPa, preferably greater than or equal to 0.1 MPa and even more preferably of between 0.2 and 1.0 MPa, so as to collect on the one hand a retentate enriched in at least one species of lanthanide, actinide or other transition metal, this species being that which is at least partially complexed with the ligand (I), and on the other hand a permeate impoverished in said species; and optionally

5

10

20

- -3 recovery of the ligand/species complexes to be separated in the retentate, and treatment of these complexes with one or more appropriate decomplexing agents so as to collect on the one hand the ligands and on the other hand the target species.
  - 2. Process according to claim 1, characterized in that the ions of the metal(s) to be separated are subjected to selective complexation.
    - 3. Process according to claim 1 or 2, characterized in that the molecular weight of the ligands (I) used is greater than the cut-off threshold of the nanofiltration membrane.
- 4. Process according to claim 1 or claim 2, characterized in that a ligand of formula (I.1) is used:

in which R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup> and R<sup>12</sup> are identical to or different from one another and are each a hydrophilic monovalent radical having the same definition as that given for R<sup>9</sup> and R<sup>10</sup> in claim 1, ethanoyl, methoxyethyl and sorbitoyl radicals being more especially preferred.

- 5. Process according to any one of claims 1 to 4, characterized in that several metal species belonging to the lanthanide and/or actinide family are separated, said separation being effected by successive complexations of the ions of each of these species to be separated, the appropriate selective ligand being chosen for each species (step 1) and a nanofiltration (step 2) and a decomplexation/collection (step 3) being carried out after each complexation.
- 6. Process according to any one of claims 1 to 5, characterized in that the nanofiltration membrane used is made of at least one material selected from the group of polymers comprising:
- polyaramides, sulfonated polysulfones, polybenzimidazolones, grafted or non-grafted polyvinyldidene fluorides, polyamides, cellulose esters, cellulose ethers, perfluorinated ionomers, associations of these polymers, and copolymers obtained from monomers of at least two of these polymers.
- 7. Process according to any one of claims 1 to 6, characterized in that the selected membrane has a cut-off threshold, expressed in g/mol, which is defined as follows:

100 - 5000 preferably 200 - 2000 and even more preferably 500 - 1500

- 8. Process according to any one of claims 1 to 7, characterized in that the pH of the medium, preferably the aqueous solution, constituting the complexation/separation medium is fixed at between 1 and 6.
  - 9. Complexing agents of the following formulae:

5

HO 
$$CO_2H$$
  $CO_2H$   $CO_2H$   $OH$ 

## Response to written opinion of 03/08/01

(I'.2)

n being between 1 and 100, preferably between 1 and 10,

Ω'·

5

10

10. Application of the process according to any one of claims 1 to 8 and of the complexing agents according to claim 9 to the production of rare earths or the processing of nuclear waste, especially that originating from the processing-recycling operations carried out on spent nuclear fuels.